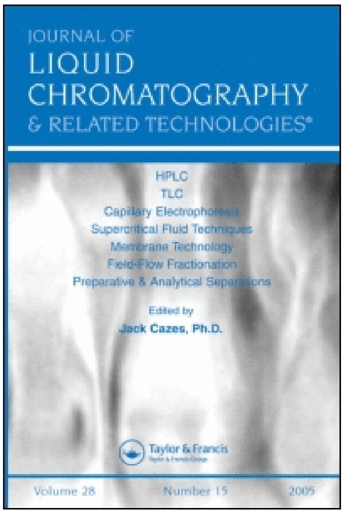

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INVESTIGATION OF CHROMATOGRAPHIC PROPERTIES OF TITANIA. II. INFLUENCE OF CALCINATION TEMPERATURE

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ABSTRACT

The characterization of calcined titanias with regard to physical properties as packing materials and crystal forms by X-ray powder diffraction, and the examination of how the ion- and ligand-exchange properties of titania shall be influenced by varying calcination temperature, were demonstrated to elucidate the relationship between the chromatographic behavior and the change of surface state accompanied with varying calcination temperature. The ligand-exchange properties in this experiment were regarded as the formation of chelate rings of 2-hydroxyl aliphatic carboxylic acids. We observed that the physical properties of titania reflected, exactly, the variation in X-ray diffraction patterns with calcination temperature. We found that only calcined titania behaving as cation-exchanger exhibited retention behavior correlated with changes in surface hydroxyl group, and that rutile formed by calcination did not behave as ion- and ligand-exchangers. The absence of these properties would account for losing the surface hydroxyl group and the coordinatively bonded water by calcination.

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INTRODUCTION

Titania has recently attracted interest as a ceramic packing materials, which possesses the desirable mechanical and physical properties of silica, and chemical stability superior to silica.[1-6] Titania has both anion- and cation-exchange properties for charged species[7-8] as well as ligand-exchange behavior towards Lewis bases, whereas silica behaves only as a cation- exchanger[8] and does not show any ligand-exchange behavior. Compared with conventional packing materials, titania exhibits completely different chemical surfaces. As the interaction of solutes with the surface of the stationary phase determines the chromatographic selectivity, a novel selectivity could be expected when using titania as packing material.

We have previously described the testing of titania, produced in our laboratory, to evaluate its ion- and ligand-exchange properties, and reported that it behaved as anion- and cation-exchanger,[9-10] and that it had the ability to recognize the position of substituent groups towards hydroxyl and other substituent aliphatic carboxylic acids on the basis of ligand-exchange.[11] In this case, the recognition of the position of hydroxyl or carboxyl group was ascribed to formation of the chelate ring. The titania retained only the carboxylic acid that was able to form a five-membered ring between titanium ion and two oxygen atoms, except bivalent carboxylic acid.

We have already prepared titania on a laboratory scale by hydrolysis and polycondensation of titanium alkoxide by the sol-gel method;[12] it was found to be anatase. Anatase is converted to rutile by heating above 700ºC. The surface state of titania would vary with increasing calcination temperature because of changing from anatase to rutile. The anion- and cation-exchange properties are thought to arise from the protonation of surface hydroxyl group in acidic pH and deprotonation of surface hydroxyl group in alkaline pH.

The coordinatively bonded water was reported to play an important role in ligand-exchange.[13] The surface hydroxyl group and the coordinatively bonded water should decrease with increasing calcination temperature. Therefore, the calcined titania at various temperatures was expected to provide retention behavior correlated with changes in surface hydroxyl group and coordinatively bonded water as well as changes from anatase to rutile.

The objective of this work was to characterize calcined titanias with regard to physical properties as packing materials and crystal forms by X-ray powder diffraction, and to examine how the ion-exchange properties and the formation of chelate rings of 2-hydroxyl aliphatic carboxylic acids on the basis of ligand-exchange of titania shall be influenced by varying calcination temperature.

Of the chromatographic behavior evaluated, we found that only calcined titania behaving as cation-exchanger exhibited retention behavior correlated with changes in surface hydroxyl group, and rutile formed by calcination did not behave as ion- and ligand-exchanger. The absence of these properties would account for losing the surface hydroxyl group and the coordinatively bonded water by calcination.

EXPERIMENTAL

Preparation and Calcination of Titania

Titania was synthesized by the method described previously,[12] by hydrolysis and polycondensation of titanium isopropylate. The titania obtained (dried at 200ºC, referred to as Ti or 200ºC in figures) was calcined in a oven for 1 hour at 300ºC, 400ºC, 500ºC, 600ºC, 700ºC, and 800ºC, respectively. The products were slurry packed in 30 mm × 4.6 mm I.D. stainless steal tubes by using 50% (w/w) aqueous methanol, respectively. After packing, the measurement of the weight of residual product allowed us to estimate roughly the density of titania and calcined titania.

Measurement of Physical Properties of Titania and Calcined Titania

Titania and calcined titania were subject to measurements for particle-size distribution, surface area, pore diameter, pore volume, and crystal form. The particle-size distribution was determined with a Coulter Multisizer II (Coulter Electronics, Luton, UK). The surface area, pore diameter, and pore volume were determined by nitrogen absorption measurement (Fuji-Silysia Chemical Ltd., Kasugai, Japan) on a laboratory-made apparatus. The X-ray powder diffraction patterns were observed by Model MXP 18 VAHF (Mac science Co. Ltd., Yokohama, Japan) to determine the crystal forms.

Evaluation of Ion-Exchange Properties of Titania and Calcined Titania

The ion-exchange properties of titania and calcined titania were evaluated by the behavior of inorganic ions. Potassium ion as a cationic solute and chloride ion as an anionic solute were prepared by dissolving with potassium chloride, potassium hydroxide, and hydrochloric acid, respectively, in pure water. Ion chromatography was performed with a Yokogawa Analytical Systems (Tokyo, Japan) model IC 500P instrument equipped with sample injector, column oven, suppresser, and conductivity detector.

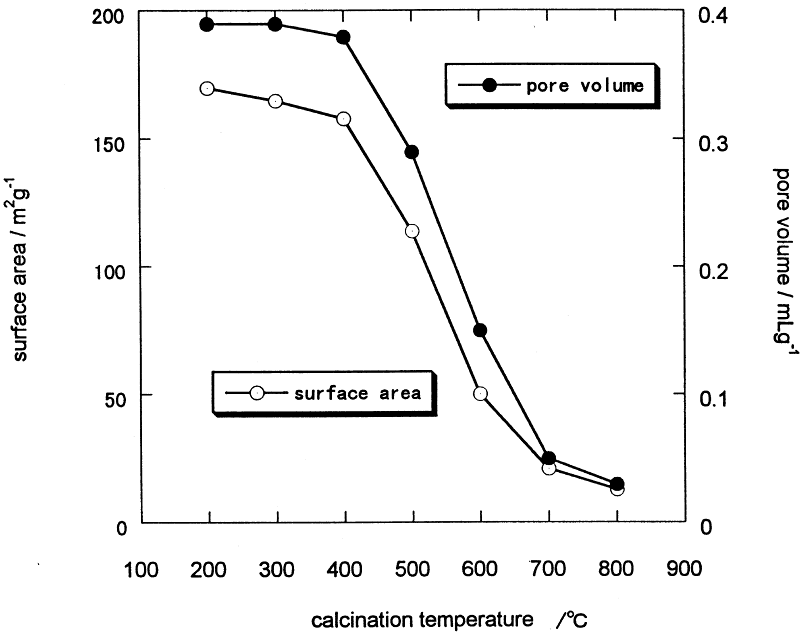

Figure 1. Change in surface area and pore volume of titania and calcined titania as a function of calcination temperature.

Table 1

Physical Properties as Packing Materials of Titania and Calcined Titania

	Calcination Temperature (°C)						
	200*	**300**	**400**	**500**	**600**	**700**	**800**
Mean particle diameter[μm]	3.17	3.31	3.75	3.30	3.22	3.65	4.19
Particle size distribution							
d_{10} [μm]	4.11	19.6	36.5	19.9	25.3	17.9	45.7
d_{90} [μm]	2.32	2.35	2.42	2.28	2.29	2.34	2.55
Density[g/cm^3]	1.1	1.1	1.1	1.2	1.7	3.6	3.6

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* Referred to as titania.

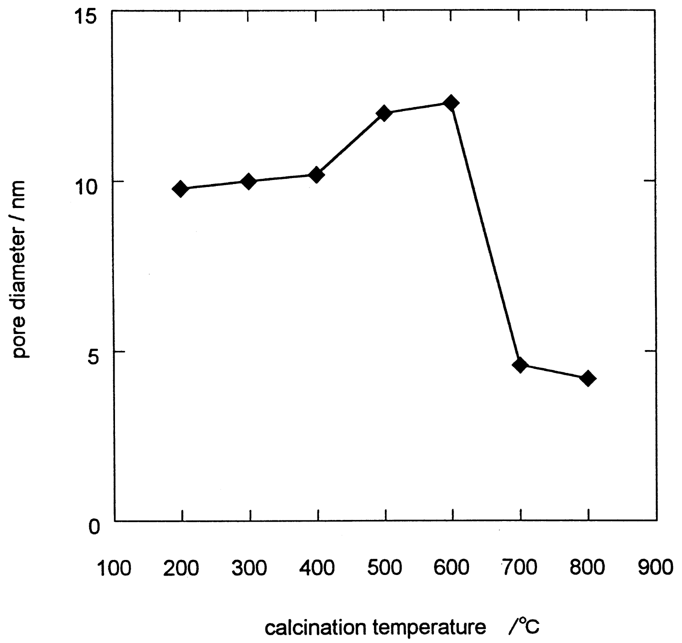

Figure 2. Change in pore diameter of titania and calcined titania as a function of calcination temperature.

The ion chromatograph was operated under the following conditions: mobile phase: 0.4 mM acetic acid-sodium acetate buffer; mobile phase flow rate: 1.0 mL min^{-1}; and column temperature: 40°C. In this experiment, suppresser was not used.

Data were processed by means of a computer running LC-100 software. The void volume was measured with D_2O in water.

Comparison of Titania and Calcined Titania on Retention Behavior of 2-Hydroxyl Aliphatic Carboxylic Acids

The stability of formation of chelate rings on the basis of ligand-exchange of titania was evaluated by using 2-hydroxyl aliphatic carboxylic acids. Carboxylic acids used as solutes were as follows: glycolic, lactic, glyceric, malic, 2-hydroxybutanoic acids. Each sample solution was prepared by diluting with water to required concentration. The ion chromatograph was operated under the following conditions: mobile phase: 0.4 mM bicine-sodium hydroxide buffer (pH 7.8, 8.6); mobile phase flow rate: 1.0 mL min^{-1}; scavenger: 5 mM sulfuric acid; scavenger flow rate: 1.0 mL min^{-1}; and column temperature: 40ºC. Data were processed by means of a computer running LC-100 software. The void volume was measured with D_2O in water.

RESULTS

Measurement of Physical Properties of Titania and Calcined Titania

The physical properties as packing materials of titania and calcined titania are summarized in Table 1, Figures 1 and 2. The density estimated roughly is shown in Table 1. The particle size distribution of calcined titania was observed in a wide variety. The density of calcined titania increased rapidly at calcination temperature above 600ºC. The surface area and mean pore volume decreased with increasing calcination temperature at a slow rate up to 400ºC, and at a much faster rate between 400 and 700ºC, again at a slow rate above 700ºC (Figure 1). In mean pore diameter, the slight increase up to 400ºC, the gradual increase from 400 to 600ºC, and the considerable decrease above 700ºC were observed (Figure 2). The series of particle size distribution of titania and calcined titania are shown in Figure 3. It is apparent that the wide particle size distribution of calcined titania resulted from two particle size fractions.

Crystal forms of titania and calcined titania were examined by X-ray powder diffraction method. The phase forms were identified on the basis of the X-ray diffraction patterns obtained and the powder diffraction files.[14] The series of X-ray diffraction patterns of titania and calcined titania are shown in Figure 4. As a result, titania showed anatase pattern, but the peaks in X-ray diffraction pattern was broad. The broad peak indicated imperfect degree of crystallization and suggested to be hydrous type. The sharpness of peaks in anatase pattern increased slightly up to calcination temperature of 400ºC, and rapidly from 500 to 600ºC. At calcination temperature of 600ºC rutile patterns arose slightly, and occupied all above 700ºC. The sharp peak indicated high degree of crystallization and loss of water in crystal.

Evaluation of Ion-Exchange Properties of Titania and Calcined Titania

Figure 5 indicates the retention behaviors of potassium ion as cationic solute and chloride ion as anionic solute on titania and calcined titania up to 600ºC. It is apparent that the retention of chloride ion decreased steeply as the pH of the mobile phase was increased, but the influence of calcination temperature on the retention of chloride ion was not very clear.

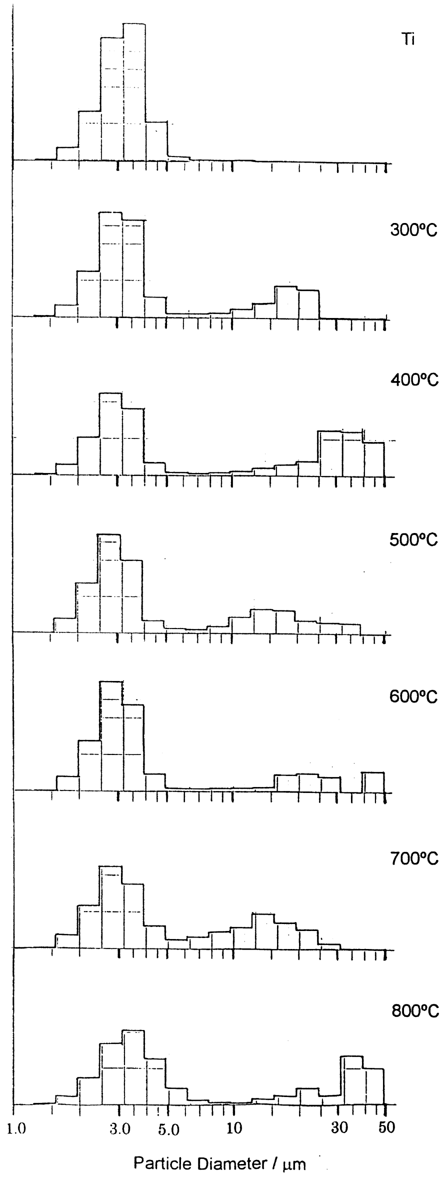

Figure 3. The series of particle size distribution of titania and calcined titania.

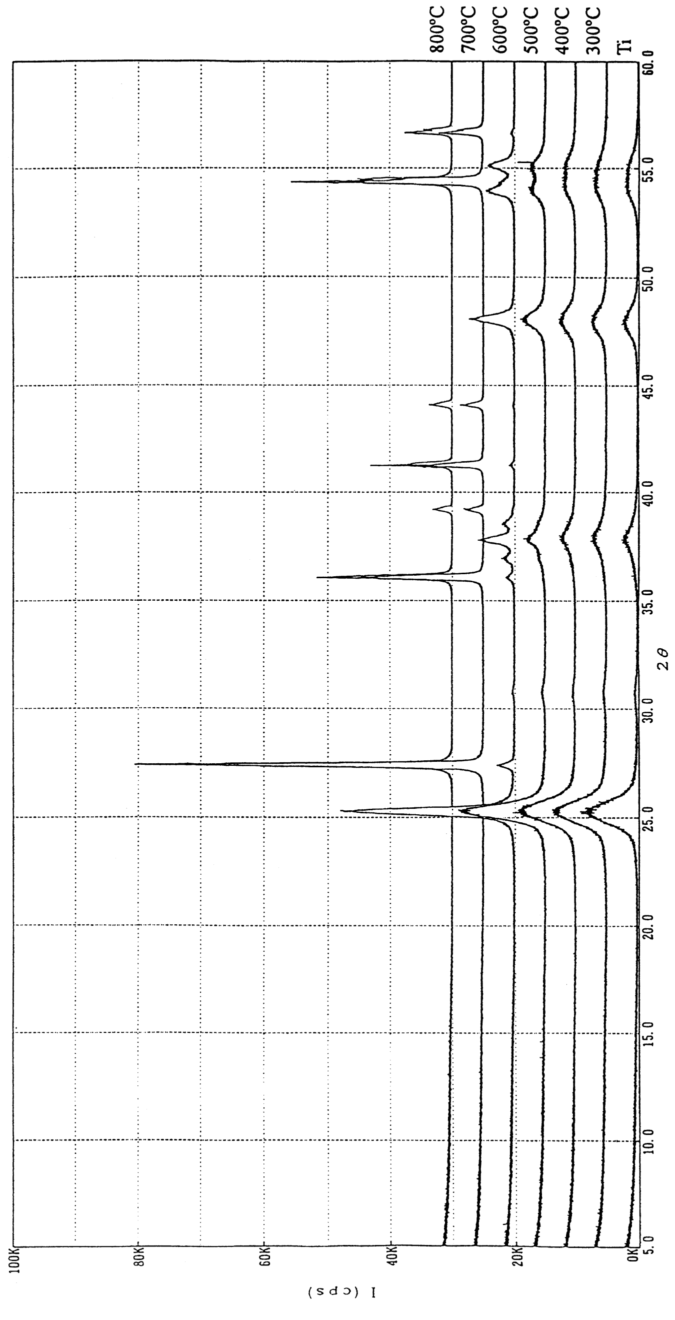

Figure 4. The series of X-ray diffraction patterns of titania and calcined titania.

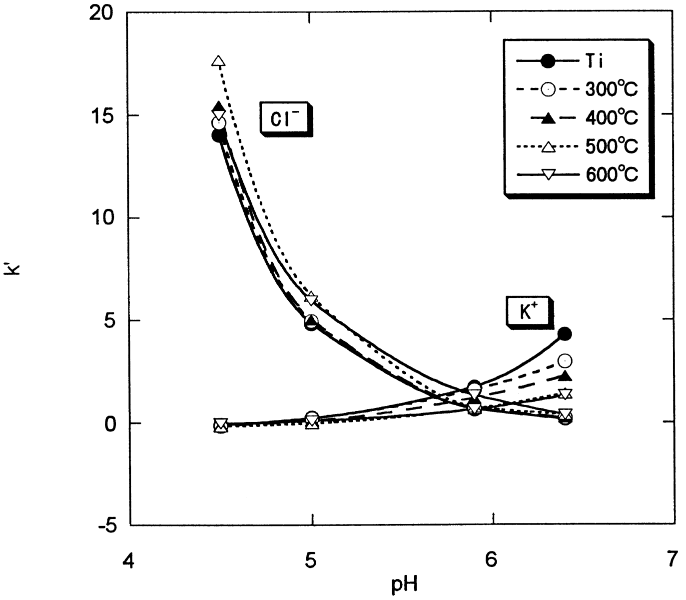

Figure 5. Dependence on mobile phase pH of the retention behaviors of potassium and chloride ions on calcined titania up to 600°C. Mobile phase: 0.4mM acetic acid-sodium acetate buffer; flow-rate: 1.0 mL min^{-1}; column temperature: 40°C; detector: conductivity detector.

The retention of potassium ion increased rapidly as the pH of the mobile phase was increased, and the value of k' decreased with increasing calcination temperature. Figure 6 indicates the retention behaviors of potassium and chloride ions on calcined titania above 700°C. It is apparent that the retention of calcined titania above 700°C was distinct from those of titania and calcined titania up to 600°C because chloride ion was slightly retained and then excluded, and the retention of potassium ion increased faintly as the pH of the mobile phase was increased.

Comparison of Titania and Calcined Titania on Retention Behavior of 2-Hydroxyl Aliphatic Carboxylic Acids

Figure 7 indicates the retention behaviors of 2-hydroxyl carboxylic acids against calcination temperature at pH8.6, that is, the relationship between the chromatographic behavior and the change of surface state accompanied with varying calcination temperature. These acids were not retained on calcined titania above 700°C as can be seen in Figure 7. The order of retention of

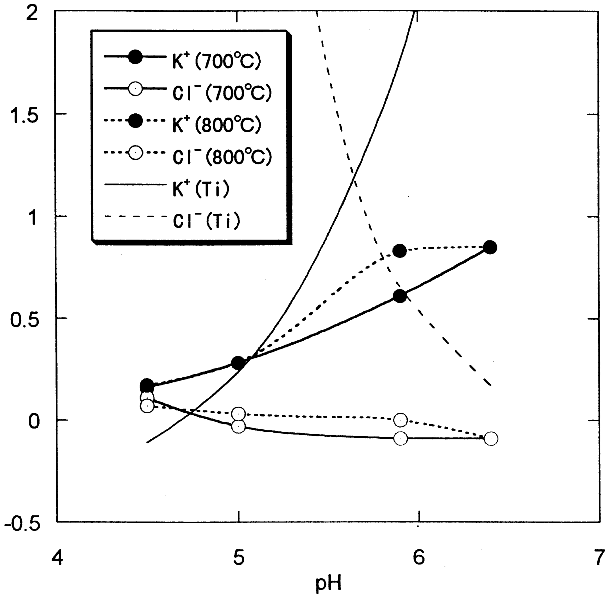

Figure 6. Dependence on mobile phase pH of the retention behaviors of potassium and chloride ions on calcined titania above 700°C. The analytical conditions are as in Figure 5.

glycolic and 2-hydroxybutanoic acids reversed at calcination temperature of 600°C. The peak of all acids reduced with increasing calcination temperature up to 600°C. The series of chromatograms of lactic acid on titania and calcined titania are shown in Figure 8.

DISCUSSION

The first research was to characterize calcined titania. To accomplish this objective we measured standard physical properties as packing materials and X-ray powder diffraction of titania and calcined titania.

From determining physical properties as packing materials, the rise of calcination temperature was found to be accompanied by a drastic decrease in surface area and porosity, by slightly enlarging up to 600°C and a steep decrease above 700°C in mean pore diameter, and a rapid increase in density above 600°C. By identifying crystal forms of calcined titania by X-ray powder diffraction, the crystal form of titania was observed to grow gradually to anatase and change completely to rutile with increasing calcination temperature.

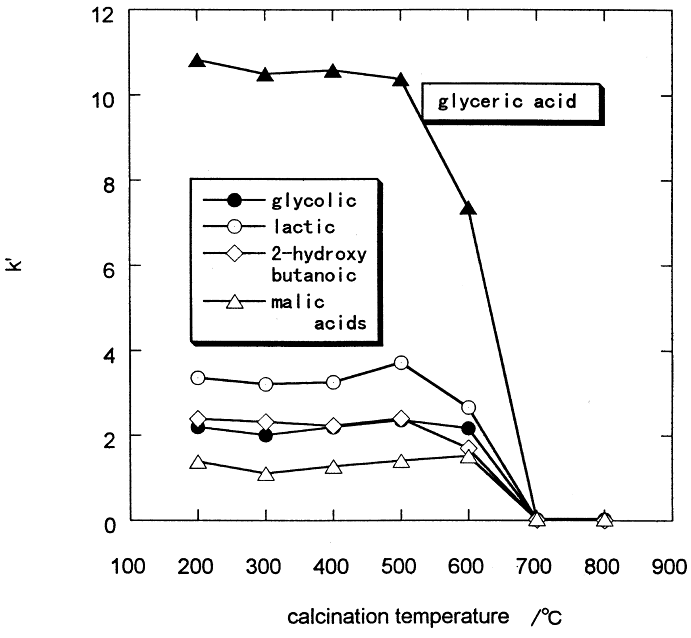

Figure 7. Dependence on calcination temperature of the retention behaviors of 2-hydroxyl carboxylic acids. Mobile phase: 0.4mM bicine-sodium hydroxide buffer(pH 8.6); flow-rate: 1.0 mL min^{-1}; column temperature: 40°C; detector: conductivity detector.

The varying from broad peaks to sharp ones indicated high degree of crystallization and losing water in crystal. This evidence was substantiated by a rapid increase in density above 600°C also. The variation in X-ray diffraction patterns was divided into three parts, the fields of calcination temperature up to 400°C, above 700°C and in between. The physical properties of titania and calcined titania were found to reflect, exactly, the variation in X-ray diffraction patterns with calcination temperature in each part. The calcination would decrease the surface hydroxyl groups that influence the ion-exchange properties, and the coordinatively bonded water that would play an important role in ligand-exchange.

The changing from anatase to rutile resulted in the differences of the bond angles and distances between a titanium ion and oxygen atoms, and the distances between two oxygen atoms in crystal structure, which should significantly influence stability of formation of a chelate ring on the surface. Thus, the retention time and elution order of 2-hydroxyl aliphatic carboxylic acids should vary in the distinct crystal form of titania.

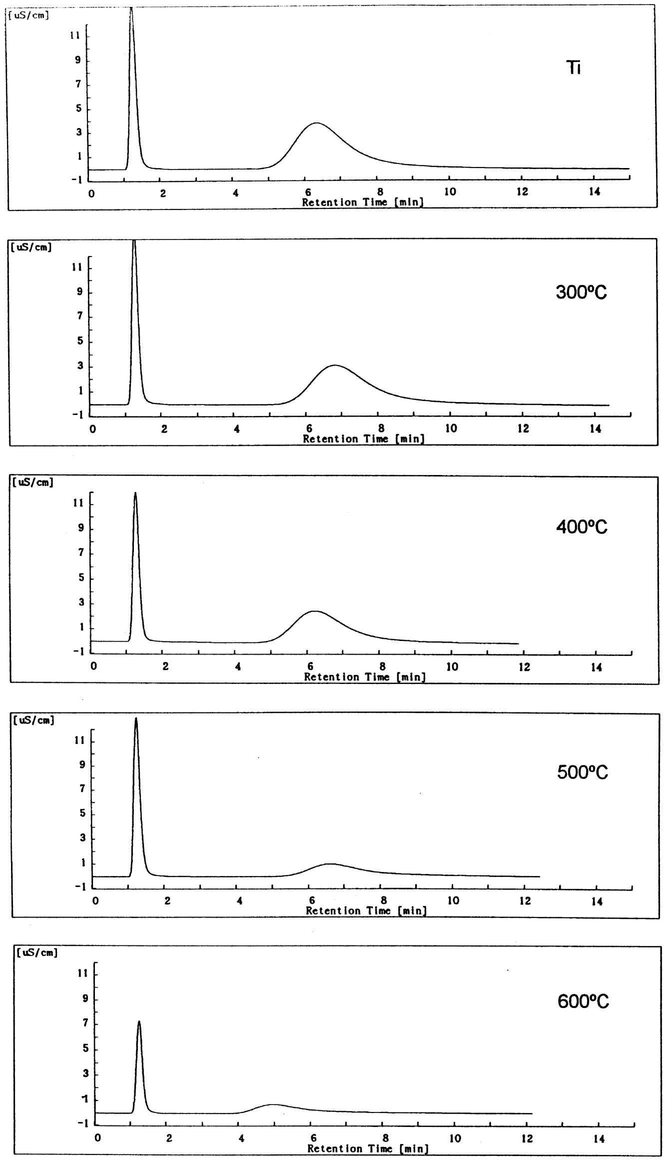

Figure 8. The series of chromatograms of lactic acid on titania and calcined titania. The analytical conditions are as in Figure 7.

Therefore, the second research was to examine how the ion- and ligand-exchange properties of titania shall be influenced by varying calcination temperature. The calcined titania up to 600ºC behaved as anion- and cation-exchanger, and the retention of potassium ion decreased with an increase in calcination temperature. The tendency suggested the retention behavior correlated with the changes in the surface hydroxyl group because surface hydroxyl groups decreased with increasing calcination temperature. On the other hand, it seemed that the retention behavior of chloride ion was independent of changes in the surface hydroxyl. This fact suggested the participation of ligand-exchange properties of titania in retention of chloride ion.

As mentioned before,[11] 2-hydroxycarboxylic acid formed five-membered rings between titanium ion and two oxygen atoms of hydroxyl group and carboxylate anion. The elution order of 2-hydroxycarboxylic acids on titania was glycolic < 2-hydroxybutanoic < lactic acid. The introduction of a substituent led to two effects, one of which was a change in basicity of donor atom, and the other was steric hindrance in formation of a chelate ring. In view of the only effect of basicity of donor atom, the retention of those was presumed to increase in the order glycolic < lactic < 2-hydroxybutanoic acid, that is, in order of increasing alkyl chain length. On the other hand, in view of the only effect of steric hindrance, the retention of those was presumed to increase in the order 2-hydroxybutanoic < lactic < glycolic acid, that is, in order of decreasing alkyl chain length. The fact that 2-hydroxybutanoic acid was less retained than lactic acid indicated it to be influenced by not only basicity of donor atom but also steric hindrance in elution order.

The elution order of 2-hydroxycarboxylic acids on calcined titania up to 500ºC was glycolic < 2-hydroxybutanoic < lactic acid. On the other hand, the elution order on calcined titania at 600ºC changed from glycolic < 2-hydroxybutanoic < lactic acid to 2-hydroxybutanoic < glycolic < lactic acid. This order suggested that the effect of steric hindrance increased in the formation of a chelate ring. It would go to prove that the changing crystal form results in the differences of the bond angles and distances between a titanium ion and oxygen atoms and the distances between two oxygen atoms in crystal structure, which shall significantly influence stability of formation of a chelate ring on the surface.

Glyceric acid was reported to form a five-membered ring between titanium ion and two oxygen atoms of two hydroxyl groups and be strongly retained on titania.[11] The similar retention behavior was observed on calcined titania up to 600ºC, but glyceric acid was more rapidly eluted on calcined titania at 600ºC than on calcined titania up to 500ºC. With regard to the formation of a chelate ring, only calcined titania at 600ºC was found to respond to the variation in X-ray diffraction patterns with calcination temperature up to 600ºC. This fact demonstrated the changing crystal form to influence stability of formation of a chelate ring on the surface of titania. The calcination temperature up to 600ºC seemed to have no influence on the retention behaviors of malic acid, which was dicarboxylic acid, namely bivalent anion. The reduction of the peak of all acids with increasing calcination temperature up to 600ºC seemed to be caused by a strong irreversible adsorption of a part of acid, but it is not explicable what the adsorption would arise from.

The calcined titania above 700ºC behaved as neither ion-exchanger nor ligand-exchanger. The absence of these properties of titania could be ascribed to losing the surface hydroxyl group and coordinatively bonded water by calcination in support of varying from broad peaks to sharp ones in X-ray diffraction patterns and a rapid increase in density.

In conclusion, the physical properties of titania reflect, exactly, the variation in X-ray diffraction patterns with calcination temperature, namely the change of surface state of titania accompanied with varying calcination temperature. With regard to ion-exchange properties of titania, the change of surface state resulted in the decreasing of surface hydroxyl groups with increasing calcination temperature, which decreased retention of potassium ion, and finally eliminated the ion-exchange properties. The retention of chloride ion seemed to participate in ligand-exchange properties of titania.

With regard to ligand-exchange properties of titania, only calcined titania at 600ºC responded to the change of crystal form accompanied with varying calcination temperature. The calcined titania above 700ºC, namely rutile, that was expected to indicate distinct behavior, did not behave as a ligand-exchanger. It is because titania lost the coordinatively bonded water by calcination. The coordinatively bonded water was found to be essential for ligand-exchange of titania. The hydroxylation of rutile surface would produce titania that has only ion-exchange properties. The titania could prove the participation of ligand-exchange properties in the retention of chloride ion.

The preparation of hydrous rutile as a packing material is expected to result in the distinct retention behavior of titania. The hydroxylation of the rutile surface and the preparation of hydrous rutile would be attempted in the near future.

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